

***p*-Anisyldiazonium Chloride and Maleimide.**—The crude product from 0.1 mole each of *p*-anisidine and maleimide was treated with acetone. There remained 3.8 g. (16%) of yellow crystals of di-*p*-anisylmaleimide (II, X = OCH₃) which were practically insoluble in acetone, benzene, ether, alcohol or chloroform. They were crystallized from a large volume of acetone. A portion of the I (X = OCH₃) was recovered from the acetone-soluble fraction by dilution with petroleum ether (60–75°). The filtrate and the crystalline material were sublimed separately at 160° (0.1 mm.). The combined solid sublimates were crystallized; yield of pure I, 29%. With two moles of *p*-anisidine per mole of maleimide, the yield of II was 35%.

In another experiment with 1.5 moles of maleimide per mole of *p*-anisidine, the crude product was hydrolyzed directly (see below) and the anhydrides were separated by distillation-sublimation. The yield of *p*-methoxyphenylmaleic anhydride was 45% and of di-*p*-methoxyphenylmaleic anhydride 6%.

***p*-Toluenediazonium Chloride and Maleimide.**—The runs with a 1:1 mole ratio are described in Table I. With 0.1 mole of *p*-toluenediazonium chloride and 0.05 mole of maleimide, the di-*p*-tolylmaleimide (II, X = CH₃) could not be isolated, since its solubility was similar to that of I (X = CH₃). Accordingly, the entire crude product was hydrolyzed (see below) and recycled by heating for 15 min. at 150–160°. The mixed anhydrides were distilled and then fractionated. The first fraction, b.p. to 145° (0.1 mm.), was *p*-tolylmaleic anhydride. The fraction boiling 145–170° (0.1 mm.) was crystallized once from methylene chloride-petroleum ether. The distillation and crystallization operations were repeated three times, giving finally 0.15 g. of pure di-*p*-tolylmaleic anhydride.

***p*-Chlorobenzenediazonium Chloride and N-Isopropylcitraconimide.**—From 0.1 mole of each reagent, the general procedure yielded 22 g. of an oily product. The oil was dissolved in ether, washed several times with water to remove acetic acid, dried and distilled. After a little forerun of unchanged N-isopropylcitraconimide, an orange-yellow oil distilled at 160–163° (0.1 mm.) (vapor temp.). Analysis of a center cut of redistilled material showed that the product was mostly N-isopropyl- α -methyl- α' -*p*-chlorophenyl- α -chlorosuccinimide (III, R = CH₃). Five grams of this product was heated briefly with 20 ml. of 2,6-lutidine near its boiling point; precipitation of 2,6-lutidine hydrochloride was rapid. The mixture was partitioned between water and ether, the excess lutidine was removed by washing with dilute acid and water, and the ether layer was dried and again distilled, b.p. 150–155° (0.1 mm.). The solid distillate (IV, R = CH₃) was recrystallized from ether-petroleum ether.

***p*-Chlorobenzenediazonium Chloride and N-Isopropylmaleimide.**—The general procedure yielded 25 g. of an oil from 0.1 mole of each reactant. The product decomposed on attempted distillation. Five grams was treated with 15 ml. of 2,6-lutidine as above and diluted with 25 ml. of benzene, giving 1.65 g. of 2,6-lutidine hydrochloride (calcd. for

pure N-isopropyl- α -*p*-chlorophenyl- α' -chlorosuccinimide (III, R = H), 2.5 g.); the oil is evidently a mixture of the latter product with I (X = Cl, R = C₆H₇). The benzene solution was partitioned between ether and water, washed free of lutidine with acid and water, dried and evaporated. The I crystallized directly and was recrystallized from ether-petroleum ether. The crystals and the mother liquors were distilled (b.p. 135–140° (0.1 mm.)) separately, combined and recrystallized.

Since the N-isopropyl derivatives are readily distilled, it may be desirable to use N-isopropylmaleimide instead of maleimide to facilitate separation from the inevitable tars. The yield of pure material seems to be enhanced.

2-Naphthalenediazonium Chloride and Maleimide.—The tarry residue obtained from 0.05 mole each of 2-naphthylamine and maleimide by the general procedure was hydrolyzed immediately with 80 ml. of 25% NaOH. After cyclization at 160–170°, the 2-naphthylmaleic anhydride was distilled. Pure 2-naphthylmaleimide was not isolated. The experiment with 1-naphthylamine was similar.

Saponification of Arylmaleimides. Arylmaleic Anhydrides.—The maleimide (either purified material or the crude product directly from the reaction) was boiled for 4–6 hours with excess 25% sodium hydroxide solution. In some cases, a little alcohol was added. After the evolution of ammonia had ceased, the mixture was diluted with water, extracted with ether and acidified with sulfuric acid. The arylmaleic acid was collected by filtration or, when quite water-soluble, by continuous ether extraction. There was no significant amount of isomerization to the arylfumaric acid⁴ during these procedures. The crude arylmaleic acid was cyclized by heating above its melting point for 10–30 min. or by refluxing for 30 min. with excess acetic anhydride followed by vacuum evaporation of the acetic acid and anhydride. If a crude maleimide was used, the anhydride was then distilled before crystallization, but this was unnecessary when starting with purified maleimide. The anhydrides were crystallized from methylene chloride-petroleum ether (60–75°) or ether-petroleum ether. Difficulty was encountered in the hydrolysis of α -*p*-nitrophenylmaleimide. Details are given in Table II.

Phenylmaleic anhydride prepared in this way (m.p. 119–120°) was identical with samples prepared by other routes.¹⁶ Our sample of *p*-chlorophenylmaleic anhydride (m.p. 149–150°) corresponded to that reported by Meerwein.³ The *p*-methoxyphenylmaleic anhydride was identical with a sample later synthesized by Miller¹⁷ by another route.

Acknowledgment.—We are indebted to the Horace H. Rackham Fund of the University of Michigan for a grant in support of this work.

ANN ARBOR, MICHIGAN

(16) C. S. Rondestvedt, Jr., and A. H. Filbey, *J. Org. Chem.*, **19**, 119 (1954).

(17) We are indebted to Dr. L. E. Miller for making the comparison and for informing us of the progress of his synthesis.

[COMMUNICATION NO. 1705 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK COMPANY]

The Structure of Certain Diphenylcyclopentenones

BY C. F. H. ALLEN AND J. A. VANALLAN

RECEIVED NOVEMBER 27, 1954

The substance long believed to be 3,4-diphenyl-3-cyclopentenone has been shown to be the 2-cyclopentenone. Certain other related structures have been corrected, including several chloroketones about which there has previously been some uncertainty.

Many years ago, while attempting to elucidate the structure of anhydroacetonebenzil (I), Japp^{1,2} carried out a reduction of the substance with hydrogen iodide, and obtained a product to which was assigned the structure 3,4-diphenyl-3-cyclo-

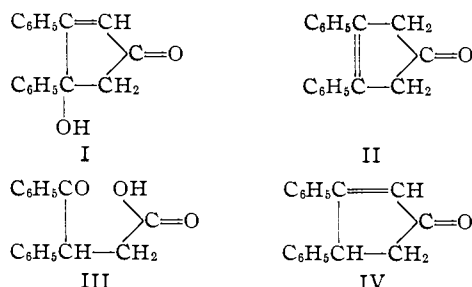
(1) F. R. Japp and C. I. Burton, *J. Chem. Soc.*, **51**, 420 (1887).

(2) F. R. Japp and G. D. Lander, *ibid.*, **71**, 123 (1897).

pentenone (II). This formulation appears to have been accepted without question ever since, in spite of certain anomalous reactions. Most outstanding of these is ozonization, which gave desylacetic acid (III).³ *A priori*, it would be expected that in a structure such as II, the two phenyl

(3) H. Burton and C. W. Shoppee, *ibid.*, 567 (1939).

groups would be held in a *cis*-relation and in the plane of the ring, a condition that is sterically unfavorable. Furthermore, one would expect that in the reduction product of I there would still be an α,β -conjugated system of double bonds, as shown in IV.



While the study of the light absorption of Japp's indanone and related compounds was under way,⁴ the reduction product of I and related diphenylcyclopentenones were also examined. The ultraviolet absorption of this diphenylcyclopentenone is very similar to those of several known α,β -unsaturated cyclopentenones (Table I), with characteristic absorption peaks in the 215 and 274 $m\mu$ regions. The latter are believed to be characteristic of α,β -unsaturated ketones conjugated with a phenyl group.⁵⁻⁷ Thus, the absorption spectra and result of ozonolysis, which are essentially unambiguous properties, favor structure IV.

TABLE I
ABSORPTION OF 2-CYCLOPENTEN-4-ONES

Compound no.	Structure	λ_{\max}		$\log \epsilon$		I.R.
		λ_{\max}	$\log \epsilon$	λ_{\max}	$\log \epsilon$	
X ⁵	3-C ₆ H ₅	284	4.35			
XI	2,3-(C ₆ H ₅) ₂ ^a	225	4.25	290	4.09	5.95
IV	3,4-(C ₆ H ₅) ₂ ^b	215	4.30	274	4.32	6.0
XII	2-CH ₃ -3,4-(C ₆ H ₅) ₂ -4-OH ^b			280	4.18	
XIII	5-CH ₃ -3,4-(C ₆ H ₅) ₂ -4-OH ^b	218	4.48	285	4.79	
XIV	2,5-(CH ₃) ₂ -3,4-(C ₆ H ₅) ₂ ^b	215	4.18	275	4.50	
XV	2,5-(C ₆ H ₅) ₂ -3,4-(C ₆ H ₅) ₂ -4-OH ^b	216	4.16	270	4.06	
XVI ⁶	2-C ₆ H ₁₁ -3-CH ₃			235	4.32	
XVII ⁷	2,3,4,5-(C ₆ H ₅) ₄			299	4.13	
VI ¹¹	3,4-(C ₆ H ₅) ₂ -4-Cl			284	4.54	
VII ¹¹	3,4-(C ₆ H ₅) ₂ -2-Cl			282	4.53	
VIII ⁹	3,4-(C ₆ H ₅) ₂ -5,5-(CH ₃) ₂ -2-Cl			283	4.51	
IX ¹²	2,3-(C ₆ H ₅) ₂ -5-Cl	228	4.50	299	4.45	

The solvent used for these determinations was (a) isoöctane; (b) methanol.

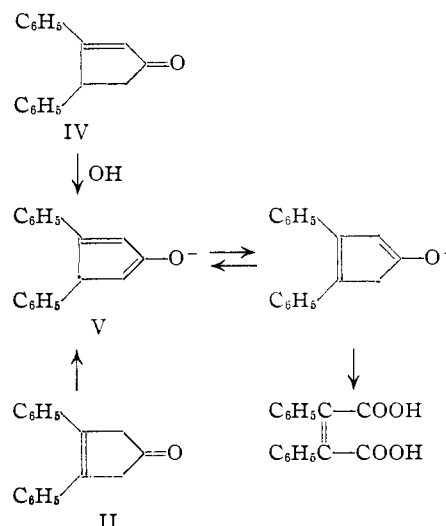
The reactions previously described that were used in assigning the incorrect structure, II, are all ionic, having been carried out in the presence of basic or acidic catalysts. For instance, sodium hypobromite oxidation, which gave diphenylmaleic acid,¹ was done in a strongly alkaline solution in which the anion V would be involved; this anion is the same for both II and IV. Further instances² are the reactions with benzaldehyde

(4) C. F. H. Allen, T. Davis, D. W. Stewart and J. A. VanAllan, *J. Org. Chem.*, **20**, 306 (1955).

(5) A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, Jr., T. L. Johnson and C. H. Shunk, *THIS JOURNAL*, **69**, 1985 (1947).

(6) R. L. Frank, P. G. Arvan, J. W. Richter and C. R. Vanneman, *ibid.*, **66**, 4 (1944).

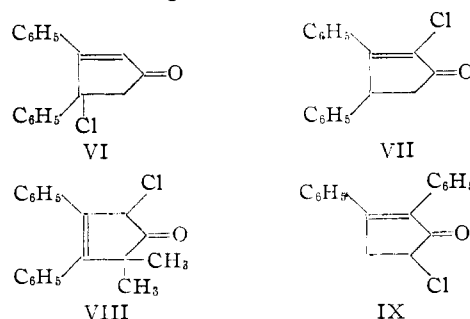
(7) N. O. V. Sonntag, S. Linder, E. I. Becker and P. E. Spierri, *ibid.*, **75**, 2283 (1953).



in acid solution, nitrosodimethylaniline in alkaline solution, and ethyl oxalate in the presence of sodium ethoxide. Such reactions are unreliable for use in proving structures.

Finally, the dehydration of 3-hydroxy-3,4-diphenylcyclopentanone may be mentioned⁸; the product was the diphenylcyclopentone, identical in properties with the one so long known, hence the structure in use was accepted, apparently without question. However, one would expect the dehydration to resemble that of the many other known analogous β -hydroxycyclopentanones which always give α,β -unsaturated ketones. In this instance, the product would have structure IV; since the latter is the one that it has just been concluded is correct, this dehydration can no longer be considered as an exception.

The spectra of certain chlorides in the diphenylcyclopentenone series, about which there has been some uncertainty, have also been examined. It is noted that the absorption of substances VI, VII and IX (Table I) are essentially alike; there is in each an α,β -unsaturated system conjugated with a phenyl group, whereas the main absorption of VIII⁹ is at 252 $m\mu$.¹⁰ It is also noteworthy that in substances IX, XI and XVII (Table I), whenever a phenyl group is on the carbon in the α -position of the conjugated system, the absorption maximum is at a slightly longer wave length; this makes it of diagnostic value.



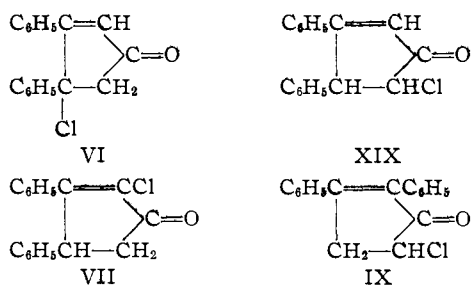
(8) H. A. Weidlich and M. Meyer-Delius, *Ber.*, **74**, 1214 (1941).

(9) C. F. H. Allen and E. W. Spanagel, *THIS JOURNAL*, **54**, 4338 (1932).

(10) This substance is considered in a subsequent paper.

Adoption of the corrected structure for 3,4-diphenyl-2-cyclopentenone makes it necessary to revise those of nearly all of its derivatives based on the previous formulation.^{1-3,8,11-13} For instance, dehydrohalogenation of 2-bromo-3,4-diphenylcyclopentanone gave II, whereas IV was expected,³ but, since the supposed II has now been shown to be IV, this falls in line.

The uncertainties among the isomeric chlorodiphenylcyclopentenones have also been cleared up; these arose many years ago, in part because erroneous structures were assigned to the starting materials, and also because of the non-recognition of ionotropic isomerizations. Three of them are α,β -unsaturated ketones, with a phenyl group on the terminal carbon atom, as shown by the ultraviolet absorption (Table I). Three structures can be written, VI, VII and XIX, of these, the



first (VI), which has been agreed upon by all interested in the field, results from the action of most active inorganic chlorides on anhydracetone-benzil.¹¹ The second (XIX), likewise accepted, is formed by chlorination of the cyclopentenone, IV.¹³ The third, known as Japp's chloride, results from the action of hydrogen chloride or hydrogen bromide¹² upon the first. By exclusion, it must have the structure VII; this has been confirmed by the formation of desylacetic acid upon ozonization. Formation of this chloride from VI by the action of hydrogen bromide in acetic acid argues against a carbonium intermediate; this isomerization may be an instance of "internal return."¹⁴

The fourth chloride is obtained by treatment of "Vorländer's ketol" with phosphoryl chloride.¹² From the position of the ultraviolet absorption maximum (Table I) of this chloride (IX), it is clear that there is an α -phenyl substituent⁴ in the unsaturated conjugated system; this rules out the structure in which a chlorine atom was located here.¹² Structure IX is therefore assigned this isomer; it is in agreement with the revised structure of the ketol (see forthcoming paper).

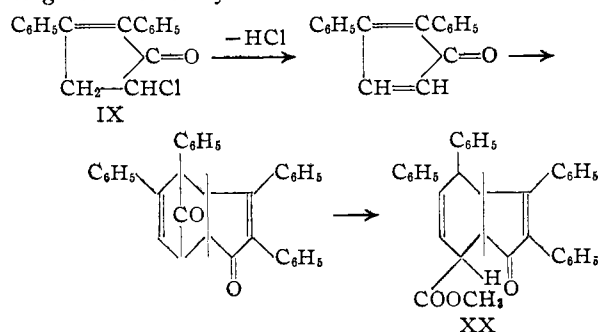
(11) C. F. H. Allen and E. W. Spanagel, *THIS JOURNAL*, **55**, 3773 (1933).

(12) C. F. H. Allen and H. Rudoff, *Can. J. Research*, **B15**, 321 (1937); D. Vorländer and M. Schrödter, *Ber.*, **36**, 1490 (1903).

(13) H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 1408 (1939).

(14) W. G. Young, S. Winstein and H. L. Goering, *THIS JOURNAL*, **73**, 1958 (1951).

Now that the structure of chloride (IX) has been established, it is obvious that the previously unknown dimeric product that results from treatment of it with sodium carbonate and methanol¹² is the indenone (XX). The reactions involved are all of well-known types¹⁵; dehydrohalogenation to a cyclic diene, dimerization of the latter to a carbonyl bridge compound, and cleavage of the bridge to give an ester by the alkali-alcohol mixture.



The four chlorides (VI, VII, VIII and IX) were treated quantitatively with methylmagnesium iodide, to see if there was any removal of chlorine, but in each case there was one addition without gas evolution. This is in line with the findings of Kohler and Tishler, namely, that with simple haloketones in which there is little hindrance to addition, all types of Grignard reagents give only addition products.¹⁶

Experimental

Ozonization of Japp's Chloride (VII).¹⁷—The ozonization proceeds extremely slowly, most of the starting material being recovered unchanged after two hours. For instance, 4.4 g. of the chloride in 100 ml. of dry ethyl acetate was treated with a current of ozone at room temperature for two hours, added, dropwise, to boiling water to expel the solvent, and precipitate an oil. This was separated (it solidified on the addition of much ice), 20 g. of sodium bicarbonate was added, and, after thorough mixing, extracted with ether. The extract, after suitable manipulation, left 3.5 g. of unchanged chloride. The bicarbonate solution was acidified, and the precipitated acid separated; benzoic acid was extracted with boiling water (a difficult separation) and 0.7 g. of desylacetic acid was collected. It melted at 156–158°, as did the authentic sample; a mixed melting point was the same. Eight other runs gave essentially the same result.

The chloride IX was practically unchanged after ozonization; only a trace of benzoic acid was isolated.

Anal. Calcd. for $\text{C}_{35}\text{H}_{28}\text{O}_3$, 7-methoxycarbonyl-3a,4,7,7a-tetrahydro-2,3,4,5-tetraphenylindenone (XX): C, 84.7; H, 5.3; CH_3O , 6.3; mol. wt., 496. Found: C, 84.7; H, 5.5; CH_3O , 6.0; mol. wt., 501.

Acknowledgment.—We are indebted to Dr. D. W. Stewart, Mr. E. E. Richardson and Miss Thelma Davis of these Laboratories for the absorption curves.

ROCHESTER, NEW YORK

(15) C. F. H. Allen, *Chem. Revs.*, **37**, 209 (1945).

(16) E. P. Kohler and M. Tishler, *THIS JOURNAL*, **57**, 218 (1935).

(17) This was done by Dr. J. H. Clark, formerly of these Laboratories, but now at the American Cyanamid Co., Stamford, Conn.